

## CHAPTER II

### BACKGROUND AND LITERATURE REVIEW

#### 2.1 Mixed Wastes

Mixed wastes are defined as wastes that contain both toxic organic and heavy metal contaminants. Mixed wastes have been generated from various sources including national laboratories and various industries. Table 2.1 shows a few samples of mixed waste generated from various sources and the major hazardous organic and inorganic constituents in mixed wastes.

**Table 2.1** Mixed waste sources and characteristics of mixed wastes

Sources of Mixed Wastes	
Power Generating Plants	Petroleum Refining Industry
Hospital/Medical Research Institutes	National Laboratories
Industrial/Municipal Incinerators	Gas Manufacturing Plant
Wood Preserving Industry	US Air Force Base
Leachate from Underground Tank/Waste-Disposal Site	

Primary Contaminants in Mixed Wastes
<u>Organics</u>
Hydrocarbon solvents: benzene, toluene, xylene, acetone, chloroform, phenols
Chlorinated compounds: methylene chloride, carbon tetrachloride, trichloroethylene
Polychlorinated biphenyls (PCBs)
Polyaromatic hydrocarbons (PAHs)
<u>Inorganics</u>
Heavy metal: Ag, As, Ba, Cd, Cr, Cu, Hg, Ni, Pb, Se, Zn
Radioactive components: $^{14}\text{C}$ , $^{60}\text{Co}$ , $^{137}\text{Ce}$ , $^{192}\text{Ir}$ , $^{90}\text{Sr}$

Toxic organics commonly found in mixed wastes are chlorinated compounds, polyaromatic hydrocarbons and hydrocarbon solvents. Heavy metals

frequently found in mixed wastes include Cd, Cr, Hg and Pb. The presence of heavy metals and toxic organics in the environment are of major concern because of their toxicity and threat to human life and the environment. Table 2.2 shows threshold limiting values (TLVs) and effects of poisoning of some important metals and toxic organics.

**Table 2.2** Threshold Limiting Values (TLVs) and effects of Poisoning of some metals and toxic organics

Metal	TLV* (mg/m <sup>3</sup> )	Effects of Poisoning
Aluminium	2	Possibly related to Alzheimer's disease
Cadmium	0.05	Destructive to membranes; nausea, vomiting; cancer; damage to lungs; kidneys
Copper	1	Destructive to membranes; nausea, vomiting
Chromium	0.5	Irritant; nausea; vomiting
Iron	1	Possible irritant; nausea; vomiting
Mercury	0.1	Irritant; nausea; vomiting; damage to nervous system, liver, kidneys
Zinc	No TLV	Nausea; vomiting

Organics	TLV* (ppm)	Effects of Poisoning
Acetone	750	Irritant; corneal clouding; damage to liver
Benzene	10	Cancer; nausea, vomiting, dizziness, narcosis, reduction in blood pressure
Chloroform	50	Cancer, irritant
Toluene	No TLV	Serious irritant
Trichloroethylene	No TLV	Cancer, narcotic, severe irritant
Xylene	100	Irritant, narcotic

\* From material safety data sheets (MSDS)

## 2.2 Adsorption of Contaminants by Natural Adsorbents

Adsorption is one of most simple, economical and efficient technique for removing contaminants. For several years, various natural adsorbents such as clay, activated carbon and zeolite have been used to remove heavy metal and organic contaminants.

The sorption of cobalt and chromium on different clays and the respective adsorption mechanisms (ion exchange or surface complex formation) were studied by Adeleye *et al.* (1995). The study revealed that the percentage of either cobalt or chromium removed in a mixed solution environment was higher than the individual adsorption in single-component experiments. This was an indication of a synergistic effect. The optimum uptake of each metal ion from mixed species was achieved by montmorillonite clay in the calcium form. Upmeier and Czurda (1997) investigated the adsorption behavior of the four natural zeolites and the clay towards different pollutants. The clay and zeolite showed similar adsorption capacities for  $\text{Cd}^{2+}$  and phenol while the adsorption capacity of the zeolite for  $\text{Tl}^{2+}$  was approximately 50 times higher than that of the clays. This demonstrated that the natural zeolite has higher potential to remove heavy metal than natural clay. Ouki and Kavannagh (1999) studied the selectivity and removal performance of clinoptilolite. They found that clinoptilolite was highly selective for lead (Pb), copper (Cu) and cadmium (Cd).

White *et al.* (1999) studied the removal of radioactive contaminants using natural zeolite as a function of temperature. This study found that cesium was more selectively sorbed than cobalt and that higher amounts of both cations were adsorbed as the temperature of contact increased.

The pH of the solution also has significant effect on the removal efficiency of natural zeolite for heavy metals. Mier *et al.* (2001) studied the interactions of Pb (II), Cd (II) and Cr (II) competing for ion exchange sites in naturally occurring clinoptilolite. The higher removal efficiencies (>95%) occurred in the acidic pH range while at high pH range (>10) the efficiency declined dramatically.

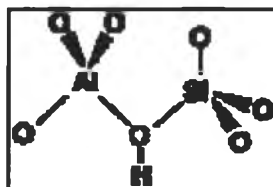
Narbaiz (1994) studied the competitive adsorption isotherms pertinent to an activated carbon adsorber treating contaminated drinking water. The water under consideration was a mixture of 1, 1, 2-trichloroethane (TCEA), used as a model toxic

compound, and the natural organic matter (NOM) from river water. This study revealed that the presence of NOM greatly reduced the adsorption capacity of TCEA. The TCEA isotherms were greatly affected by the initial concentration of both solutes; the adsorption capacity of the NOM was reduced by a maximum of 5-10% because of the TCEA. This was possibly the result of adsorption, which involved competition in only a fraction of adsorption sites. Derakhshan (1999) studied the adsorption capacity of activated carbons for the removal of phenol and aniline contaminants from wastewater. The experimental results indicated that phenol was adsorbed less effectively onto the activated carbons than aniline, this was believed to be due to aniline's slightly basic nature and hence its attraction to acidic surfaces. Clinoptilolite has also been applied to remove toxic organics. Sismanoglu and Pura (2001) have studied the adsorption of ortho-, meta- and para-nitrophenols on clinoptilolite. Their study showed that the adsorption of aqueous nitrophenols on clinoptilolite was a function of the solution concentration and temperature.

### **2.3 Natural Zeolite**

Zeolites form in nature as a result of the chemical reaction between volcanic glass (ash) and saline water. The natural reaction temperature range is from 27°C to 55°C, and the pH is typically between 9 and 10. Nature requires 50 to 50,000 years to complete the reaction.

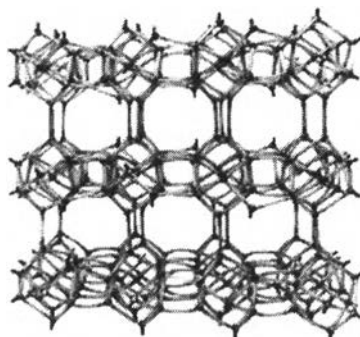
Natural zeolite minerals can be defined as crystalline, hydrated aluminosilicates of alkaline and alkaline-earth cations that consist of infinite or finite three dimensional crystal structures of (Si, Al)O<sub>4</sub> tetrahedra, which are linked together by the sharing of oxygen atoms as shown in Figure 2.1. Their structure contains channels and pores filled with a certain amount of water and exchangeable cations. This water can evaporate when the zeolite heated to about 250°C and is regained at room temperature; also some of cations constituent may be exchangeable from the zeolite inner cavities and pores without any major change of zeolite structure.



**Figure 2.1** Primary building unit of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedral.

Cronstedt first discovered zeolite minerals in Sweden in 1756, and gave them their name, which comes from the Greek word meaning the “boiling stones”. Since that time, nearly 50 naturally occurring zeolites have been identified, the most common of which are analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, and phillipsite. In addition, more than 150 zeolite types have been synthesized.

Clinoptilolite is not the most well known, but is one of the more useful of the natural zeolites. Clinoptilolite has been used in many applications such as a chemical sieve, a gas absorber, a feed additive and an odor control agent as a water filter for municipal and residential drinking water and aquariums. Clinoptilolite exists in extensive deposits throughout the world. Clinoptilolite is well suited for these applications due to its large amount of pore space, high resistance to extreme temperatures and chemically neutral basic structure. The clinoptilolite framework model is shown in Figure 2.2.



**Figure 2.2** Clinoptilolite framework model view along cleavage plane of crystal plates.

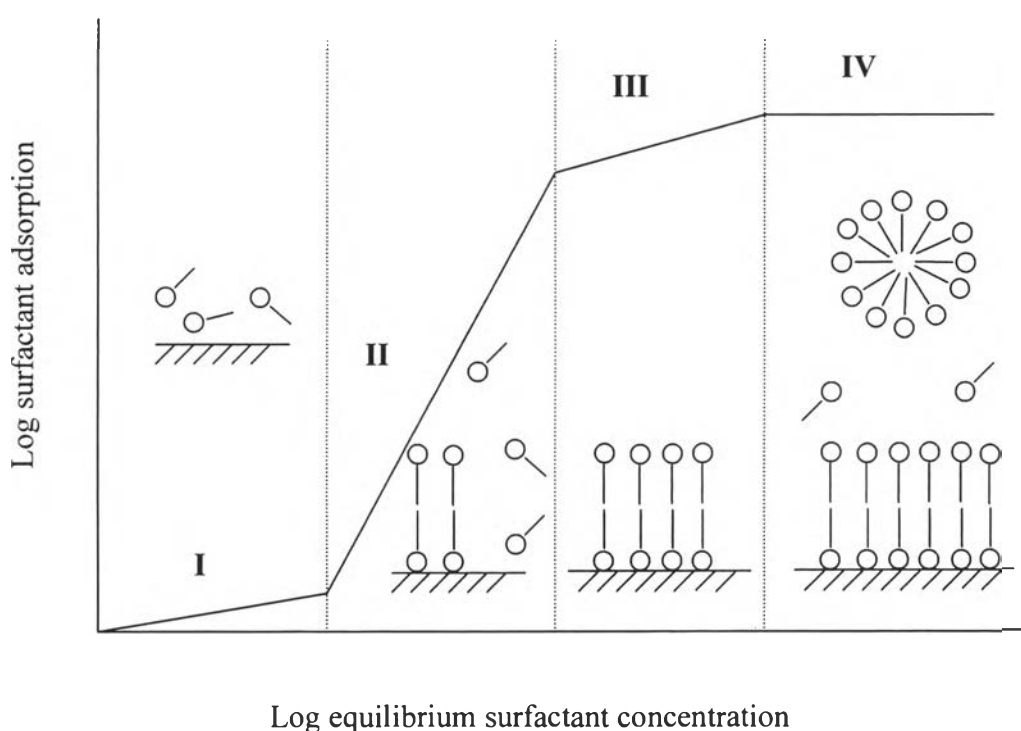
The simplified formula of clinoptilolite is,  $(\text{Na,K})_6\text{Si}_{30}\text{Al}_6\text{O}_{72}\cdot n\text{H}_2\text{O}$ . The structure of clinoptilolite is Si and Al ordering within the tetrahedral framework structure. Every oxygen is connected to either a silicon or an aluminum ion (at ratio of  $[\text{Al}+\text{Si}]/\text{O} = 1/2$ ), and there is a sheet-like structural organization. A few bonds that are widely separated from each other connect the sheets to each other. The sheets contain open rings of alternating eight and ten sides. These rings stack together from sheet to sheet to form channels throughout the crystal structure. The size of these channels controls the size of molecules or ions that can pass through them, allowing clinoptilolite to be used as a chemical sieve (i.e., allowing some ions to pass through while blocking others). The excess oxygen in the alumina molecules gives the framework a negative charge. This charge and the open framework allows the clinoptilolite to trap positively-charged ions (cations) such as sodium ( $\text{Na}^{1+}$ ), potassium ( $\text{K}^{1+}$ ), calcium ( $\text{Ca}^{2+}$ ) and/or magnesium ( $\text{Mg}^{2+}$ ).

Clinoptilolite has a high cation exchange capacity thus allowing an efficient removal of heavy-metal cations. The high cation exchange capacity results from the unique crystal structure of zeolite minerals which basically is formed by a framework of  $\text{SiO}_4^-$  tetrahedral, wherein all oxygen atoms are shared by two adjacent tetrahedra resulting in an overall oxygen/silicon ratio of 2:1. The characteristic isomorphic substitution of silicon by aluminum in the tetrahedral-sites results in a net negative charge of the framework, which is balanced by loosely bound, exchangeable, cations, mainly of the alkali and alkaline earth elements. The cation exchange capacity (CEC) for the clinoptilolite and clay are 2.6 and 0.8 meq/g, respectively.

The cation exchange behavior, which controls the selectivity for particular cations in exchange processes, depends on the charge and size of the cations and the structural characteristics of the particular zeolite mineral e.g. channel dimensions. Clinoptilolite thus has the potential to remove both toxic organic and heavy metal contaminants. However, the problems for using natural zeolites are as follow; products contain a variety of impurities and low organics sorption capacity. So the enhanced organics sorption capacity by surfactant-modified clinoptilolite was investigated.

## 2.4 Surfactant Adsorption onto Natural Adsorbents

The adsorption isotherm of an ionic surfactant onto an oppositely charged substrate is typically S-shaped when plot between the log of adsorbed surfactant density and the log of the equilibrium concentration of surfactant (Scamehorn *et al.*, 1982). The isotherm can be divided into four regions, as shown in Figure 2.3.



**Figure 2.3** Typical adsorption isotherm of surfactant on solid oxide surface.

Region I is low adsorption of surfactant on the substrate. The surfactant adsorbs mainly by ion exchange, possibly with the hydrophobic group more or less prone on the substrate. This region does not have lateral interactions between the adsorbed surfactant molecules.

In region II there is a rapid increase in adsorption of surfactant, resulting from interaction of the hydrophobic chains of oncoming surfactant ions with those of previously adsorbed surfactant and with themselves. The aggregation of these adsorbed surfactants has been called hemimicelle or admicelle, depending on their

morphology. The hemimicelle is a monolayer structure having the head group adsorbed on the surface while the tail is in contact with the aqueous phase. In this adsorption region the original charge of the solid is neutralized by the adsorption of oppositely charged surfactant ions. The admicelle is a bilayer structure with a lower layer of head groups adsorbed on the substrate surface and an upper layer of head groups in contact with solution, so that the solid surface has acquired a charge of the same sign as the surfactant ion. The point of transition from region I to region II, representing the first formation of adsorbed surfactant aggregates, is called the hemimicelle concentration (HMC) or critical admicelle concentration (CAC).

In region III, the adsorption of surfactant increases more slowly with concentration than in region II because adsorption now must overcome electrostatic repulsion between the oncoming ions and the similarly charged solid.

Region IV is a region where the adsorption reaches a plateau either because the surface has become saturated with admicelles or because the surfactant concentration in the solution has reached the CMC of the surfactant. At the CMC, the first micelle forms at the same chemical potential as the last admicelle forms. When the surfactant concentration is increased further, the chemical potential is the same as the first micelle to form and thus produce more micelles without an increase in the adsorption of more surfactant.

Cations (Na, K) adsorbed on the surface of natural adsorbents can be replaced by cationic surfactant. Cationic surfactants, showing a strong affinity to the exchange sites at the zeolite surfaces, take the place of exchangeable metal cations and thereby form a layer covering the zeolite surface. Only the external surface of the zeolite is accessible for the large surfactant molecules. So the external surface becomes electrically neutral or even positively charged as a consequence of the surfactant loading either in a monolayer or in a bilayer, respectively. However, the internal surfaces still remain an active cation exchanger. (Chen *et al.*, 1992)

Li (1999) investigated the sorption kinetics of hexadecyltrimethylammonium (HDTMA) on natural clinoptilolite. The amount of sorbed HDTMA is a function of the initial HDTMA input and the sorption time. When the initial HDTMA input is less than the external cation-exchange capacity of the clinoptilolite,



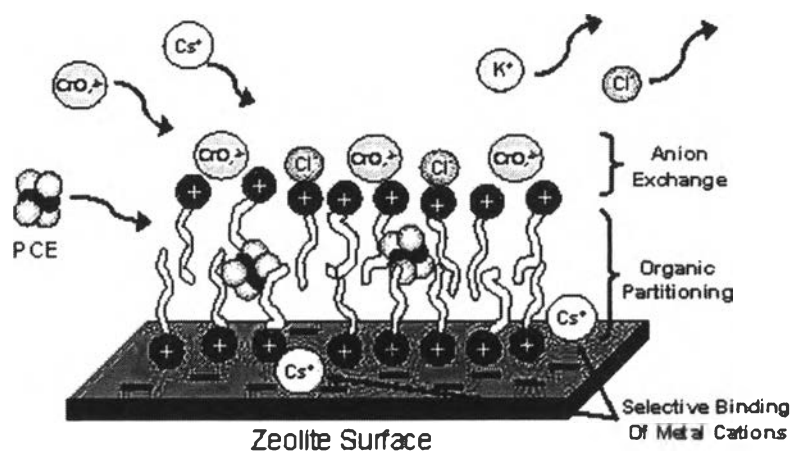
the HDTMA sorption is fast and equilibrium can be established in 1 hour. As the initial HDTMA input is greater than the external cation-exchange capacity of clinoptilolite, which will result in more than a monolayer HDTMA surface coverage, the time for HDTMA sorption to reach equilibrium increase exponentially. The counterion concentrations suggest that, at the initial stage of adsorption, HDTMA molecules sorb on the zeolite via micelle forms, which is manifested by a decrease in chloride solution concentration with time. When the HDTMA solution concentration is depleted to less than its critical micelle concentration, the adsorbed micelles rearrange themselves to a more stable monolayer or bilayer configuration, which is reflected by an increase in counterion solution concentration due to desorption of chloride from admicelles.

In addition, the Tapping-Mode Atomic Force Microscopy (TMAFM) and High-Resolution Thermo gravimetric (HR-TGA) have also been used to study the patterns of hexadecyltrimethylammonium bromide (HDTMA) sorption on the treated surface. The results indicate that the buildup of HDTMA bilayer or some form of a bilayer begins before full monolayer coverage is completed (Sullivan *et al.*, 1998).

The chemical and biological stability of surfactant-modified zeolite or SMZ was studied by Li *et al.* (1998). Under acidic conditions, desorption of HDTMA was negligible. Under basic conditions, desorption was negligible when  $\text{Cl}^-$  was the HDTMA counterion, while desorption was 15% when  $\text{Br}^-$  was the counterion. This indicated that more desorption occurred when  $\text{Br}^-$  was the counterion than when  $\text{Cl}^-$  was the counterion, except for the low ionic strength cases, where more HDTMA desorption occurred. The result also suggested that only monomer desorbed from the sorbed bilayer, and that the amount of monomer desorbed depends on the anion concentration in solution. This would explain why more HDTMA desorbed when SMZ was equilibrated with water than with higher ionic strength solutions. The results of the SMZ toxicity experiments indicated that the bacteria remained viable in all the microcosms with SMZ. In those microcosms containing aqueous HDTMA without zeolite, HDTMA inhibited the growth of the microorganism.

## 2.5 Use of Surfactant-Modified Zeolite to Adsorb Toxic Organics and Heavy Metals

Sorption of the quaternary amine in bilayer or admicelle form is causing the charge on surface to change from negative charge to positive and the organic carbon content of the zeolite to increase. The positive surface charge provides sites for sorption of anions such as chromate and nitrate. The organic-rich surface layer provides a partitioning medium for sorption of nonpolar organics such as chlorinated solvents and fuel components. Inorganic cations such as  $\text{Cs}^+$  can bind to cation exchange sites on the internal zeolite surfaces, or be selectively bound on external surface sites as shown in Figure 2.4.



**Figure 2.4** Schematic diagram of sorption mechanisms for anions, cations, and nonpolar organics on SMZ (Bowman *et al.*, 1997).

Cadena and Bowman (1994) investigated the mechanism of anion sorption such as chromate by hexadecyl-trimethylammonium-modified zeolite. The results showed that the maximum chromate sorption appears to occur when zeolite is treated to 100% of its external cation-exchange capacity. Bromide was used as counterion for HDTMA-modified zeolite in their study. Desorption of bromide was found to be approximately linear with increasing chromate sorption. The proportion of bromide desorbed was almost twice the quantity of chromate sorbed. Moreover, they also found that the presence of inorganic pollutant such as  $\text{Pb}^{2+}$  and organic pollutant such

as BTX (Benzene, Toluene and Xylene) together in the same solution did not diminish the ability of HDTMA-zeolite to retain either class of compound. The results indicated that HDTMA-zeolite has much potential for treatment of waters contaminated with mixtures of pollutants of widely varying chemistries.

Counterions have significant effects on the HDTMA sorption on zeolite, the chromate adsorption on cationic-treated zeolite, and the stabilizing of the sorbed cationic bilayer. The HDTMA sorption capacity on zeolite follows  $\text{Br}^- > \text{Cl}^- > \text{HSO}_4^-$ . In contrast, the chromate sorption capacity follows  $\text{HSO}_4^- > \text{Br}^- > \text{Cl}^-$ , thus indicating that the exchangeability of the counterion is more important than the total HDTMA loading in controlling the amount of chromate adsorbed by HDTMA-treated zeolite. HDTMA-Br-treated-zeolite was shown to be more practicable (Li and Bowman, 1997).

Li *et al.* (1998) studied sorption of oxyanions by surfactant-modified zeolite. The results showed that the best oxyanion sorption will be achieved when the initial surfactant concentration is much greater than the CMC and surfactant loading is twice of the zeolite external cation exchange capacity to ensure complete bilayer formation. Sorption of oxyanions onto SMZ is due to surface anion exchange, so that competing ions such as sulfate lower sorption of target anions such as chromate. Additionally, increasing ionic strength inhibits oxyanion sorption.

Sorption of ionizable organic solutes by SMZ was studied by Li *et al.* (2000). The results of this study demonstrate that sorption of organic contaminants increased when increased surfactant loading up to equivalent monolayer coverage (100 mmol/kg). Beyond monolayer coverage, further increases in surfactant loading did not enhance sorption of organic contaminants at neutral pH. On the other hand, the sorption of the ionizable organic compounds such as phenol and aniline varied as function of both pH and surfactant loading on the zeolite. When solution pH is such that the neutral form of an ionizable species dominates, no sorption enhancement occurs in treating the SMZ beyond monolayer coverage. At pH values where ionized species are important, sorption to SMZ at bilayer coverage will be enhanced or depressed depending upon the ionic charge.

Li and Bowman (1998) studied the sorption of perchloroethylene (PCE) by SMZ as controlled by surfactant loading. The sorption of PCE on SMZ through

partitioning of PCE into the organic phase was formed by the surfactant on the zeolite surface. The PCE sorption coefficient on SMZ is a function of the surfactant loading and resultant organic phase density. At below full monolayer coverage and higher surfactant loading levels, the PCE sorption is most effective. In bilayer, PCE sorption efficiency decreases due to increased density of the hydrophobic core of the sorbed surfactant bilayer. The results revealed the greater hydrophobicity of the monolayer-versus the bilayer-modified surface might be a result of the greater PCE sorption efficiency exhibited by the monolayer systems.

Saengchote (2003) was the first to study the adsorption of organic and heavy metal pollutants on SMZ modified by using a two-step surface modification technique. The resulting SMZ was shown to selectively adsorb heavy metal ions such as cadmium ( $\text{Cd}^{2+}$ ) from aqueous solution. Moreover the highly hydrophobic surface of SMZ also provided effective sorption sites for organic contaminants such as toluene. The adsorption capacity of SMZ decreased slightly where both  $\text{Cd}^{2+}$  and toluene are removed simultaneously in mixed system.

## 2.6 Regeneration of SMZ

Although SMZ has shown to have the potential to remove various types of contaminants, SMZ has a finite sorption capacity for different contaminants. Successful regeneration of SMZ appears to be the key factor for its applications in waste treatment. Li and Bowman (1999) studied the regeneration of SMZ after saturation with contaminants. They have shown that the SMZ can be treated with carbonate solution where chromate was replaced by carbonate and/or hydroxide anions can regenerate chromate-saturated SMZ. By rinsing with HCl solution, the carbonate sorbed on surfactant bilayer reacts with protons to form  $\text{CO}_2$  that escape from the surface and solution, leaving  $\text{Cl}^-$  as the counterion. However, the production of  $\text{CO}_2$  gas decreased the hydraulic conductivity, resulting in no further drainage under gravity. Thus, this method was not a practical regeneration scheme. An alternative method was also studied by using sodium dithionite solution to reduce Cr (VI) to Cr (III). Reduction of chromate to Cr (III) frees up anion exchange sites for further chromate sorption. The cationic Cr (III) is likely strongly bound to the

SMZ by cation exchange and/or precipitation as hydroxides. Early breakthrough was found after regeneration by sodium dithionite solution. The behavior of the dithionite-regenerated material suggests a decrease in chromate sorption affinity and/or change in hydraulic properties of the SMZ that result in increased hydrodynamic dispersion. The results also showed that PCE-saturated SMZ could be fully regenerated by air stripping.

Changing the pH of the solution is an alternative method to regenerate surfactant-modified adsorbents. Malakul *et al.* (1998) found that the adsorption of metal ions into modified-clay complexes has a strong pH-dependence. For the cadmium adsorption by the modified-clay complexes, it was found that high metal adsorption capacity could be obtained at pH 7, while there is negligible metal adsorption at pH 3. For the copper adsorption, it was found that no copper uptake was experienced at pH 3 while at pH 8 copper ions are adsorbed strongly. These results suggested that the adsorption of metal ions on surfactant-modified adsorbents is a reversible process. The shift of pH from high to low values can be used to transform the adsorbents from a state of “high” affinity for metal ions (adsorption) to one of “low” affinity (desorption). Thus changing the pH of the solution can conveniently be used to regenerate surfactant-modified adsorbents.

Recently, biodegradation has been explored as a means to remove organic contaminants that adsorb on SMZ. Sorption of nonpolar organic compounds on SMZ is reversible. By sorbing such contaminants, the solution concentration is lowered so that the contaminants become less toxic to degrading organisms. The sorbed organics are slowly released as they are microbially degraded. Fuierer *et al.* (2000) tested the hypothesis that a reactive nutrient- and electron acceptor-enhanced microbial support system could be placed in a zone of subsurface contamination and thereby stimulate biodegradation of an organic contaminant such as toluene. The microbial support system was comprised of SMZ. Furthermore, the SMZ could be pre-loaded with nitrogen and phosphate as nutrients. Batch isotherms experimentals were used to determine the toluene sorption capacity of raw and nutrient-loaded SMZ. They showed that the sorption of toluene on both materials was similar. Aerobic batch slurry experiments were conducted to determine the rate of toluene degradation and microbial growth in a SMZ support system. These experiments showed that aerobic

biodegradation occurred in the presence of both raw and nutrient-amended SMZ. In addition, the use of nutrient-amended SMZ eliminated the need to add nutrients to the system. However, biodegradation occurred at a slower rate in the presence of SMZ than in the solution-only cultures, and at an even slower rate in the presence of nutrient-amended SMZ. Assuming biodegradation only takes place in solution, the rate of biodegradation in the presence of SMZ/nutrient-amended SMZ will be influenced, and perhaps limited, by the rate of desorption.